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Procedia Environmental Sciences 16 (2012) 125 – 130

Procedia Environmental Sciences

The 7th International Conference on Waste Management and Technology

Preparation and characterization of lignin-containing nanofibrillar cellulose

Xuan Wang, Xiaoxia Cui, Liping Zhang*

College of Material Science and Technology, Beijing Forestry University, No. 35 Tsinghua esat road, Beijing 100083, China

Abstract

Cellulosic nanofibrillar structures had received much attention because of its wide range of distribution, renewable and environmentally benign nature and perfect mechanical properties. However, as an important component of plant fibres, lignin was always removed in paper making process. The waste water contained lignin had caused a serious environmental problem. So it was important to study the application of lignin. In this study, different lignin-containing Kraft wood pulps were obtained after different chemical treatments. The raw materials were pre-treated through the process of acid hydrolysis and then the pulps were homogenized by a high-pressure homogenizer. After the above processes, nanofibers of different lignin-containing cellulose samples dispersed in deionised water were obtained. The samples were characterized by XRD, TEM and thermal analysis. The results obviously showed the nanosize and crystallinity of different lignin-containing cellulose through the TEM and XRD analysis. The hydrophilicity of lignin-containing nanofibrillar cellulose samples were evaluated by contact angle measurements. The experimental results indicated that the lignin-containing nanofibrillar cellulose has hydrophobic property to some extent.Click here and insert your abstract text.

Keywords: lignin-containing; nanofibrillar cellulose (NFC), characterization, preparation

1. Introduction

Lignin, a three-dimensional amorphous polymer consisting of methoxylated phenyl-propane structures, is essential to the life of vascular plants. However, isolated lignin is industrially manufactured as an organic waste stream in the pulp and paper industry and in biomass conversion processes for biofuel

* Corresponding author. Tel.: +86 13911868160
E-mail address: wsx5480070@163.com, zhanglp418@163.com

doi:10.1016/j.proenv.2012.10.017

production. Only a small part of this amorphous polyphe-nolic macromolecule is used in tailored material applications [1, 2].

Lignin is particularly interesting as it is a waste product from the paper industry. Previous work has shown that lignin can be used as an additive in composite fabrication [3]. Nina Graupner [4] applied the lignin as a natural adhesion promoter in biodegradable, thermoplastic cotton fibre-reinforced composites. M.D.H. Beg [5] adopt the lignin to reinforced PP composites and so on. Lignin can impart beneficial properties to the structure of composite.

Nowadays, using Kraft wood pulp to produce NFC (cellulose contains lignin) is not common to see. NFC has far better mechanical properties than a majority of the commonly used reinforcement materials. Today, NFC is not commercially available; instead Kraft wood pulp which is a closely related item is commercially available [6].

The goal of this work was to produce and characterize of NFC nanocomposites. In this paper, NFC dispersing in deionised water was prepared from Kraft wood pulp board using chemical and physical treatment

2. Experimental Procedures

2.1. Material

Kraft wood pulp boards obtained after different chemical treatments and a thermo-mechanical pulp were obtained from pulp mill in Beijing and were used as received. The pulp boards were dried at 105℃ for 6h before used.

2.2. Preparation of suspension of NFC in deionized water

After the pre-treatment of the Kraft wood pulp board in diluted sulphuric acid (25%) at a constant mixing speed for 4
hours at 85℃. The Kraft wood suspension was vacuum filtered, and the cake was washed first with deionized waterto remove the $H^+$and $SO4^{2-}$ until the filter liquor reached a pH of 7. The cake was immersed into deionized water. After the Kraft wood was suspended in deionized water, the suspension was homogenized at a high pressure of 60 MPa for 20 times. The NFC dispersing in deionised water was obtained. Two kinds of NFC samples were prepared with the lignin content of 5% and 10%

2.3. Performance and characterization

The crystallinity of the nanofibrillar cellulose, NFC (5% lignin) and NFC (10% lignin) was evaluated by SHIMADZU XRD-6000 operating at 40kV/30mA with a Cu Kα radiation (wavelength, λ=0.154 nm). The samples were scanned at 2 deg/min under the diffraction angle 2θ ranging from 5 ° to 40 °.

The NFC was examined with a HITACHI H-600 transmission electron microscope (TEM) at an acceleration voltage of 80 kV. To examine the NFC, one droplet of 0.01 % diluted suspension was put on a Cu-grid. To enhance contrast in TEM, the NFC was negatively stained with a 2 wt% aqueous solution of phosphotungstic acid for 1 min.

Thermal gravimetric analysis (TGA) was performed using a SHIMADZU TGA-60 from 30 °C to 600 °C at a heating rate of 20 °C /min under a nitrogen flow. Approximately 20 mg of material was used.

The water contact angle of pure nanofibrillar cellulose, NFC (5% lignin) and NFC (10% lignin) films were analysed using a determinator of water contact angle made in Shang Hai.

3. Results and Discussion

3.1. Crystallinity

XRD, FTIR and ^{13}C NMR spectroscopy were most common used methods for the characterization of cellulose structure. XRD gave the most direct results such as crystallinity. In this study, the samples crystallinity was defined as the ratio of the amount of crystalline cellulose to the total amount of the sample materials. Fig 1 showed cellulose XRD patterns for pure nanofibrillar cellulose, NFC (5% lignin) and NFC (10%). The strongest peak, at 2θ=22.6 °, originates from the cellulose crystalline plane 002 [7, 8]. The intensities of peaks were decreased with the increase of lignin in cellulose. The trough at 2θ=16.2 ° was considered as the amorphous, which disappeared after the chemical pre-treatment. When lignin was existed in cellulose, the crystallinity of cellulose will decrease in theory. From the Fig 1 we knew that the crystallinity of cellulose with lignin also maintained at a high level of over 54%. So, through high pressure homogenization, the NFC could also have good properties.

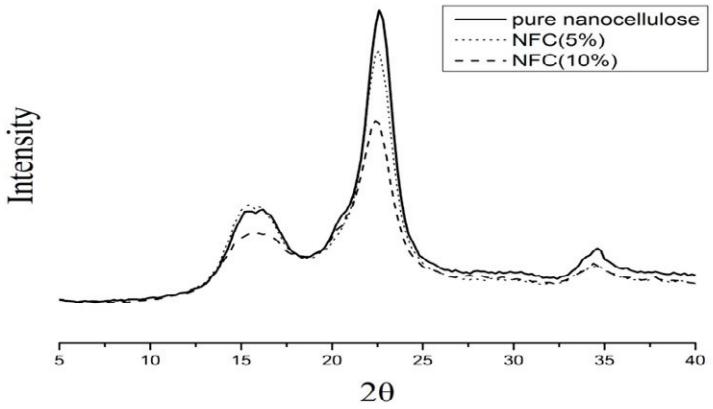

Fig 1 X-ray diffraction of pure cellulose nanofibrillar, NFC (5%) and NFC (10%)

3.2. Morphology of NFC

Fig 2 shows the TEM image of NFC. From Fig 2, we can see that the NFC has a rod-like structure. It has formed a good link between lignin and cellulose. The Fig also shows the shape and size distribution of NFC, which has a diameters of 0.2μm and lengths up to several micrometers. Treatment with dilute sulphuric acid can effectively break down the amorphous cellulose. Thus liberating crystalline cellulose into the suspension. And after homogenization, the lignin containing nanofibrillar cellulose was distributed separately. The reason may be that diluted sulphuric acid permeated into the micro fibril that make the interaction among nanofibrils lower and can be separated by the high shear and high impact [9].under the high ratio of amplification, we can clear see the lattice of NFC, this can be further indicate that NFC should be obtained by Acid hydrolysis.

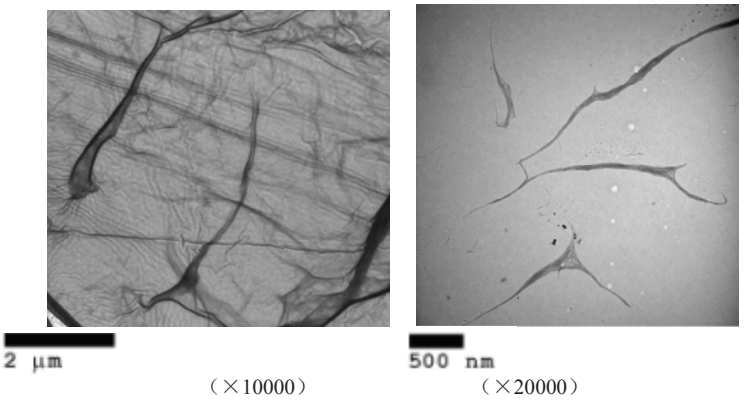

Fig 2 TEM images of NFC

3.3. Thermal gravimetric analysis

The thermal gravimetric curves of pure nanofibrillar cellulose, NFC (5% lignin) and NFC (10%) were displayed in Fig 3. On account of the difference in constitution, the samples normally decomposed at different temperature.

It can be seen that the initial decomposing temperature of pure nanofibrillar cellulose, NFC (5%) and NFC (10%) is 335,333 and 305 °C from thermal gravimetric analysis (TGA) curves in Fig. 3. The decomposing temperature of pure nanocellulose was higher than NFC because of the higher crystallinity. While the decomposing temperature of NFC just decreased by 2°C compared with pure nanocellulose. The reason may be that the lignin could have formed hydrogen bonds with cellulose. In the temperature range from 400 to 600 °C the residual weight of NFC (5%) is more than pure nanocellulose from TGA curves. It also can explain the bonds between lignin and cellulose.

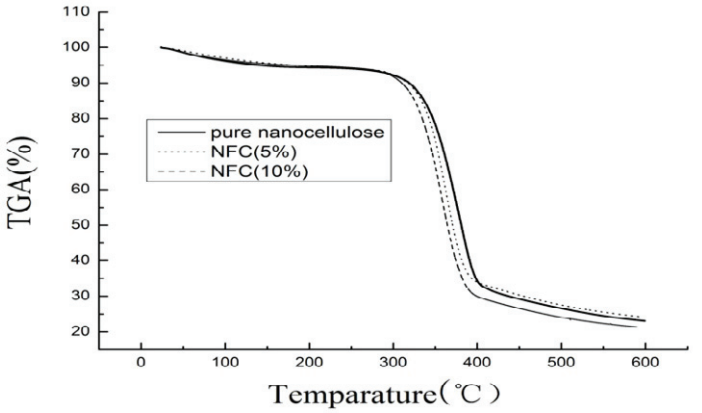

Fig 3 TGA curves of pure nanofibrillar cellulose, NFC (5% lignin) and NFC (10%)

3.4. Water contact angle

It can be seen that the initial contact angle of cellulose with different lignin content were different in Fig 4. With the increasing of lignin content, the initial contact angle of cellulose had increased obviously. Because of the hydrophobic property of lignin, the lignin-containing cellulose was influenced to become one kind of hydrophobic composite to some extent. The lignin was well-distributed in the surface of cellulose; the lignin also had some bonds to cellulose such as hydrogen bond and so on.

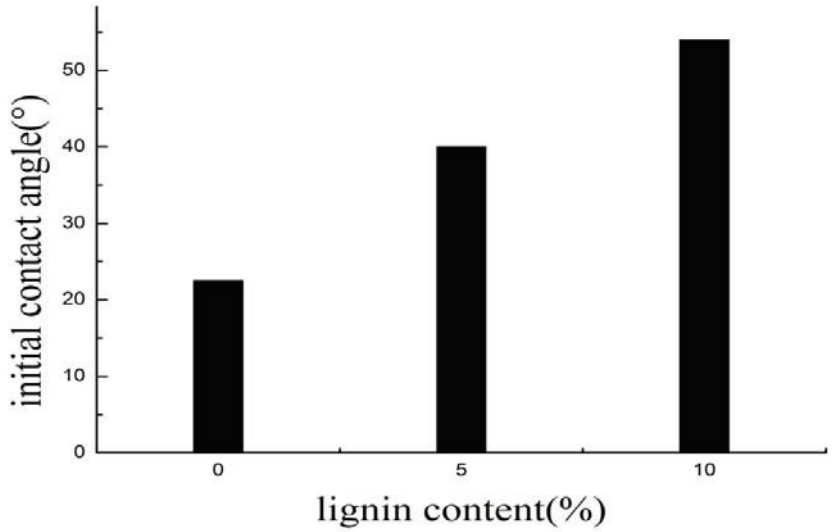

Fig 4 The initial contact angle of pure cellulose, NFC with lignin content of 5% and 10%

4. Conclusion

TGA, XRD, and TEM were used to study the properties and structure of the NFC. The increases in total amorphous character of the cellulose decrease the relative degree of crystallinity because of the existing of lignin. After chemical and physical treatment, the NFC in the length of several micrometers and diameters ranging from 100-200 nm was obtained. The initial decomposing temperature pure nanocellulose was little higher than NFC. The water contact angle of NFC indicated that the lignin-containing cellulose had hydrophobic property to some extent compared to pure cellulose. The result tells us that the NFC could have good compatibility to polymer matrix while making composites. It also increased the mechanical properties of polymer composites to a great extent.

Acknowledgement

We thank for the financial supports of Doctoral Fund of Ministry of Education of China (20110014110012) and Beijing Natural Science Foundation (2112031).

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